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Electronic Properties of $CsSnBr_3$: Studies by Experiment and Theory

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In this paper, the band structure of cubic and tetragonal phases of $CsSnBr_3$ has been investigated by temperature-dependent UPS and XPS in conjunction with *ab initio* calculations. The calculated results show that when $CsSnBr_3$ changes from a cubic phase to a tetragonal phase, the conduction and valence bands show slight changes accordingly. The density of states of Br (4s and 4p) in the valence band increases with the phase transition from cubic to tetragonal, whereas those of Cs and Sn show almost no changes. Both cubic and tetragonal phases of $CsSnBr_3$ show semiconductor character with bandgaps near the Fermi levels. The bandgap of the cubic phase at R k-point is calculated to be 0.42 eV, whereas those of the tetragonal phase at the A k-point are 0.41, 0.40 and 0.35 eV for c/a = 1.01, c/a = 1.02 and c/a = 1.04, respectively. The calculated results are in agreement with UPS and XPS measurements, and indicate direct correlation between the electronic structure and structural phase transitions.

KEYWORDS: $CsSnBr_3$; UPS; XPS; *ab initio* calculation; phase transition

INTRODUCTION

Many perovskite crystals (ABX_3) undergo phase transitions in which they transform to structures slightly distorted from the original crystals. The perovskite crystal $CsSnBr_3$ undergoes three successive phase transitions at $T = 19$, 1 and $-26\,^{\circ}C$. The crystal symmetry sequentially transforms from cubic to tetragonal to monoclinic with decreasing temperature.[1] It is well known that these phase transitions are caused by the condensation of normal modes of the phonons below the transition temperature. In particular, most of these phase transitions are caused by condensation of the zone-boundary mode associated with rotation of the BX_6 octahedron.[1] The microscopic electronic origin of the structural phase transitions has not been made clear in the perovskite system, and there is insufficient experimental evidence to show that the electronic structure directly correlates with such structural phase transitions.

Although the band structure of cubic $CsSnBr_3$ have been investigated by several groups,[2–4] the band structure of the other phases of $CsSnBr_3$, such as the tetragonal and monoclinic phases, is relatively unknown. Questions such as changes in the electronic structure of $CsSnBr_3$ as it undergoes structural phase transition still remain unresolved. It is thus important to examine the electronic properties of different phase structures in order to understand the relation between the electronic structure transitions and the structural phase transitions. The purpose of the present work is to clarify this relation by studying the evolution of valence band structures under the different structural phases, using temperature-dependent UPS and XPS in conjunction with *ab initio* calculations. The results show how the electronic structure of $CsSnBr_3$ changes when it undergoes phase transitions.

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EXPERIMENTAL

Valence band XPS and UPS measurements of $CsSnBr_3$ at different temperatures were made in a VG Escalab MkII spectrometer using Mg Kα (1253.6 eV) and He I (21.22 eV) sources, respectively. The pressure inside the analytical chamber was maintained at $<10^{-9}$ mbar. The Mg anode was operated at 120 W. The electron energy analyser was equipped with a triple channeltron detector and its pass energy was kept at 10 eV. All spectra were obtained at a photoemission angle of 75° with respect to the sample surface.

AB INITIO CALCULATIONS

An *ab initio* band structure calculation for the cubic and tetragonal phases of $CsSnBr_3$ was performed by the linear-muffin-tin orbital (LMTO) method with the atomic sphere approximation (ASA). This calculation, based on the local density approximation (LDA) within the density-functional theory, is charge self-consistent. In order to provide an adequate description of the charge density and potential in interstitial regions, 12 empty spheres have been added at suitable sites, while preserving the crystal symmetry. The ratio of atomic radii for Cs, Sn and Br and the empty sphere is 2.595 : 1.7 : 1.6 : 1.0, according to Ref. 4. We have also used different numbers of empty spheres, such as eight atoms to test the accuracy of the calculation, and found the differences in the results to be

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very small. The special k-point method[5] is adopted for summation over the Brillouin zone.

RESULTS AND DISCUSSIONS

Band structure of simple cubic $CsSnBr_3$

The atomic positions of $CsSnBr_3$ in simple cubic structure are shown in Fig. 1 and the calculated band structure of the simple cubic phase (lattice constant = 0.5804 nm)[4] is shown in Fig. 2. It can be seen that there is a bandgap near the Fermi level, and that the smallest bandgap is at the R k-point. This calculation shows cubic $CsSnBr_3$ to be a narrow-gap semiconductor, which agrees with the theoretical calculation by Rose *et al.*,[4] but is different from the previous calculations by Parry *et al.*[2] and Lefebvre *et al.*[3] Using empirical tight-binding calculations, Perry *et al.* found the compound to be semimetallic, whereas Lefebvre *et al.* obtained a zero-gap semiconductor by an empirical pseudopotential method. Similar to the results of Rose *et al.*, we also find that the cubic symmetry of the compound does not prohibit the appearance of an energy gap. In our calculation, the LDA bandgap of this compound at different high symmetry points is obtained as follows: 2.19 eV at point Γ, 2.08 eV at point X, 1.68 eV at point M and 0.42 eV at point R. Considering that LDA underestimates the energy gap in semiconductors, the actual bandgap should be larger than this calculation, so that this phase of the compound should be semiconducting rather than semimetallic.

Evolution of electronic structure during structural phase transition

The perovskite crystal $CsSnBr_3$ exists in a simple cubic phase with a lattice constant of 0.5804 nm at >292 K. With decreasing temperatures, the *c*-axis suffers a small distortion and the structure turns into the tetragonal phase. Scaife *et al.*[6] had found that $CsSnBr_3$ exhibited a tetragonal phase with $a = 1.159$ nm and $c = 1.161$ nm in a tetragonal cell by powder x-ray diffraction at 285 K. To study the evolution of the electronic structure via structural phase transition, we consider the tetragonal phase of $CsSnBr_3$ using four sets of lattice parameters for a five-atom unit cell: $c/a = 1.00$, $a = 0.5804$ nm; $c/a = 1.01$, $a = 0.578478$ nm; $c/a = 1.02$, $a = 0.57658$ nm; $c/a = 1.04$, $a = 0.57286$ nm. We have found that $c/a = 1.02$ and $a = 0.57658$ nm is the optimized equilibrium lattice set by total energy calculation. The calculated band structure of the tetragonal phase is plotted in Fig. 3 for $c/a = 1.00$ and $c/a = 1.02$.

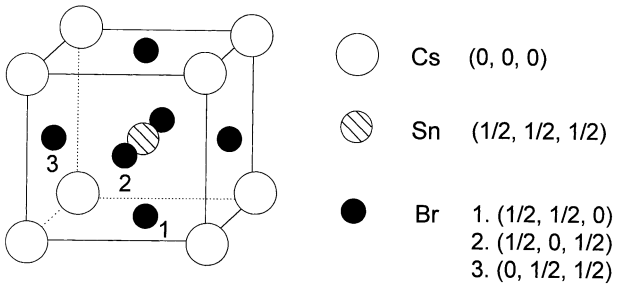

Figure 1. The atomic positions of $CsSnBr_3$ in simple cubic structure.

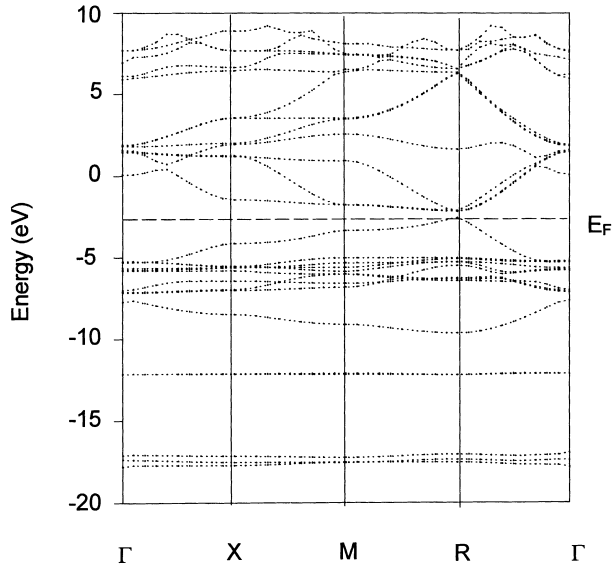

Figure 2. Band structure of simple cubic $CsSnBr_3$ as calculated by LMTO-ASA (lattice constant = 0.5804 nm).

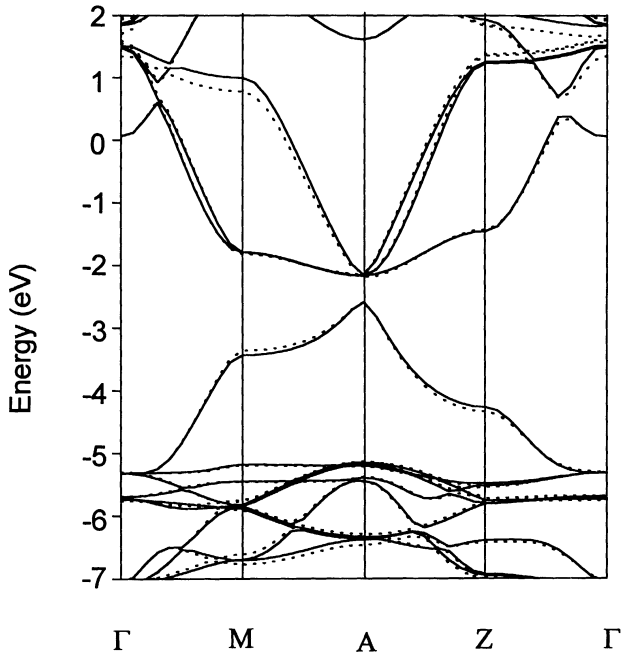

Figure 3. Calculated band structure of tetragonal $CsSnBr_3$ ($c/a = 1.02$, $a = 0.57658$ nm) (dotted line). The solid line is for the cubic phase ($c/a = 1$, $a = 0.5804$ nm), which is plotted for comparison with the tetragonal cell. The band structure of the phase with lattice parameters of $c/a = 1.01$ and $a = 0.578478$ nm is not shown in the figure because it falls between those for $c/a = 1$ and $c/a = 1.02$.

The calculated results indicate a fall in the conduction band and a rise in the valence band near the Fermi level with increasing distortion along the *z*-direction of the tetragonal phase. Both cubic and tetragonal phases of $CsSnBr_3$ appear to be narrow-bandgap semiconductors with bandgaps found at point A (point R for the cubic phase) of 0.42 eV (for $c/a = 1.00$), 0.41 eV (for $c/a = 1.01$), 0.40 eV (for $c/a = 1.02$) and 0.35 eV (for $c/a = 1.04$). It can also be seen from Fig. 3 that the changes in band structure occur differently along different symmetry axes or for different energy levels.

Experimental results of valence band obtained by UPS and XPS

Figure 4 shows the UPS and XPS (valence band) spectra of $CsSnBr_3$ at room temperature. There are three main peaks in the UPS and XPS spectrum at −4 eV, −10 eV and −15 eV from E_F, which are associated with Br 4p, Cs 5p and Br 4s, respectively. Two other peaks at −2 eV and −7 eV are found in the XPS spectrum, which can be assigned to Sn 5s.

The calculated density-of-states (DOS) results (shown in Fig. 5) show that during the phase change from cubic to tetragonal the DOS of Br (4s, 4p) in the valence band increases, whereas those of Cs and Sn show almost no change. These are theoretical results for the ideal case at 0 K, neglecting temperature effects. The UPS spectrum from a real material is of course different from the ideal case. It would contain information from both a pure electronic phase transition (ideal case) and temperature effects. The intensity of UPS peaks is expected to decrease with decreasing temperature (shown in Fig. 6). Thus, comparing the DOS curve with UPS spectra at different temperatures is not a simple matter.[4] Many other effects make the comparison even more complicated, such as matrix elements, excitation and surface effects, as well as the experimental difficulty in determining the Fermi level exactly. To compensate for the temperature effect on the UPS intensity, we use the peak intensity ratios instead. In this way, it can be seen that the ratio of Br 4p/Cs 5p for 27 °C is larger than that at 15 °C, which is in agreement with theoretical results. As for the Br 4s peak (−15 eV), it is near the region of secondary electron emission, so its intensity is strongly masked by the secondary electron intensity and is too complex to be discussed in this paper.

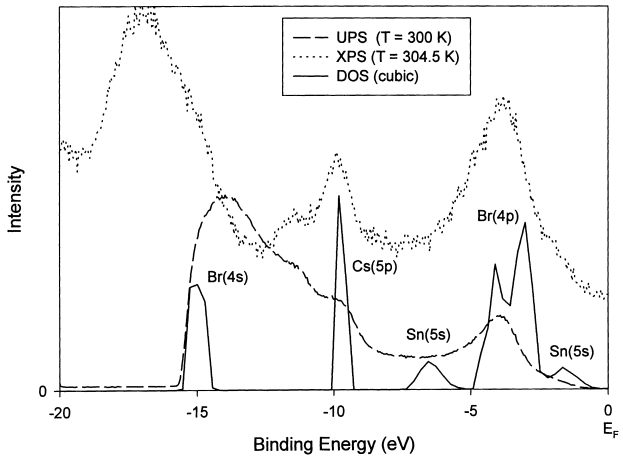

Figure 4. The UPS and XPS (valence band) spectra of $CsSnBr_3$ at room temperature. The calculated total density of states (DOS) of cubic (dashed line) $CsSnBr_3$ by LMTO-ASA is also shown.

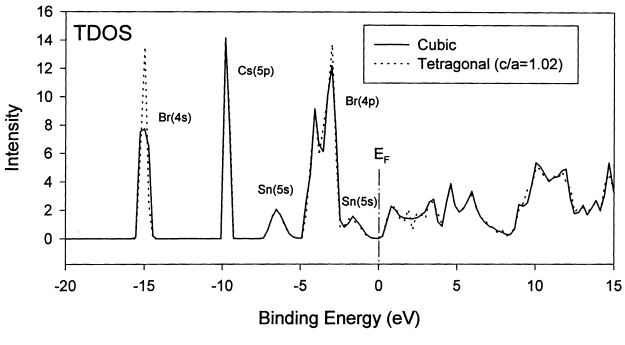

Figure 5. Density of states (DOS) of $CsSnBr_3$. The solid line is for the cubic phase and the dashed line is for the tetragonal phase ($c/a = 1.02$). The DOS of Br 4p and Br 4s in the valence band of the cubic phase is larger than that of the tetragonal phase, but the DOS of Cs 5p is almost unchanged.

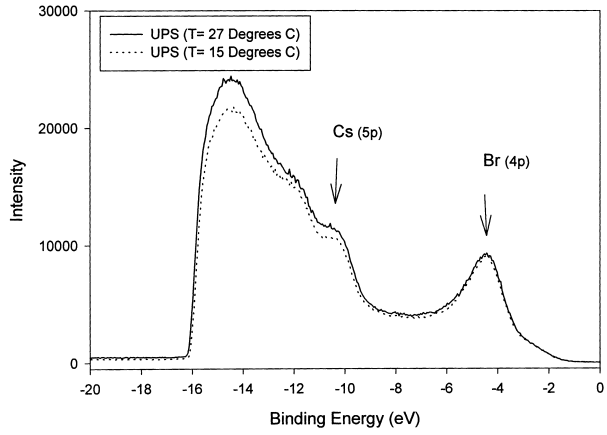

Figure 6. The UPS spectra of $CsSnBr_3$ obtained at different temperatures. The solid line was obtained at 27 °C and the dotted line was obtained at 15 °C.

Because the phase transitions are associated with the freezing of rotational modes of the $SnBr_6$ octahedron around the three principal axes, the valence and core levels of Br atoms should be greatly affected by the phase transitions. These observations are consistent with our other temperature-dependent UPS and XPS measurements and theoretical calculations.

CONCLUSIONS

In this paper, the band structure of cubic and tetragonal phases of $CsSnBr_3$ has been investigated by temperature-dependent UPS and XPS in conjunction with *ab initio* calculations. Structural phase changes associated with the $SnBr_6$ octahedron can be seen to affect the electronic structure of the Br 4s and Br 4p valence bands. Both cubic and tetragonal phases of $CsSnBr_3$ show semiconductor character with bandgaps near the Fermi level. The calculated DOS results are in agreement with UPS and XPS measurements.

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